Pre-Lithiation of High-Capacity Battery Electrodes

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Stanford University

June 13, 2019

Project ID
bat272

Overview

Timeline

- Start: August 1, 2017
- End: October 31, 2020
- Percent complete: 60%

Budget

- Total project funding
  $900k from DOE
- Funding for FY18
  $300k
- Funding for FY19
  $300k

Barriers

Barriers of prelithiation

- Low Coulombic efficiency
- Low capacity
- High chemical reactivity

Targets: high-efficiency and high-energy batteries

Partners

- Collaboration
  - BATT program PI's
  - SLAC: In-situ X-ray
  - Amprius Inc.
  - Stanford: Zhenan Bao

Project Objective and Relevance

Objective

-Design and synthesize lithiated silicon to prelithiate various anode materials.

-Increase first-cycle Coulombic efficiency via anode prelithiation.

-Increase first-cycle Coulombic efficiency via cathode prelithiation.

-Increase the stability of prelithiation reagents in both dry air and ambient air conditions.

-Design and fabricate fully lithiated anode materials to pair with high capacity lithium-free cathodes for next generation high energy density batteries.

Milestones for FY18 and 19

Month/year	Milestones
1/2018	Develop Li-containing anodes with excellent electrochemical and environmental stability (completed)
4/2018	Develop Li-containing anodes with excellent rate capability (completed)
7/2018	Develop Li-containing anodes with excellent cycling stability for Li-S full cell (completed)
10/2018	Fabricate free-standing LixSn/graphene or LixAl/graphene foil as an alternative to lithium metal anodes (completed)
1/2019	Demonstrate anode prelithiation reagent with specific capacity >900 mAh/g with stability in ambient air (completed)
4/2019	Demonstrate anode prelithiation process to be compatible with a variety of solvent processing (on track)

Approach/Strategy

Prelithiation reagents design and synthesis

1) Compensate 1st cycle anode capacity loss with anode prelithiation reagents (Li_xSi nanoparticles)
2) Compensate the anode capacity loss with cathode prelithiation reagents (Li_2O/metal nanocomposite)
3) Achieve improved stability of anode prelithiation reagents in the dry and ambient air condition by exploring inorganic and organic coatings, such as Li_2O, LiF and artificial SEI-coating.
4) Increase the stability of cathode prelithiation reagents by exploring different composites

Structure and property characterization

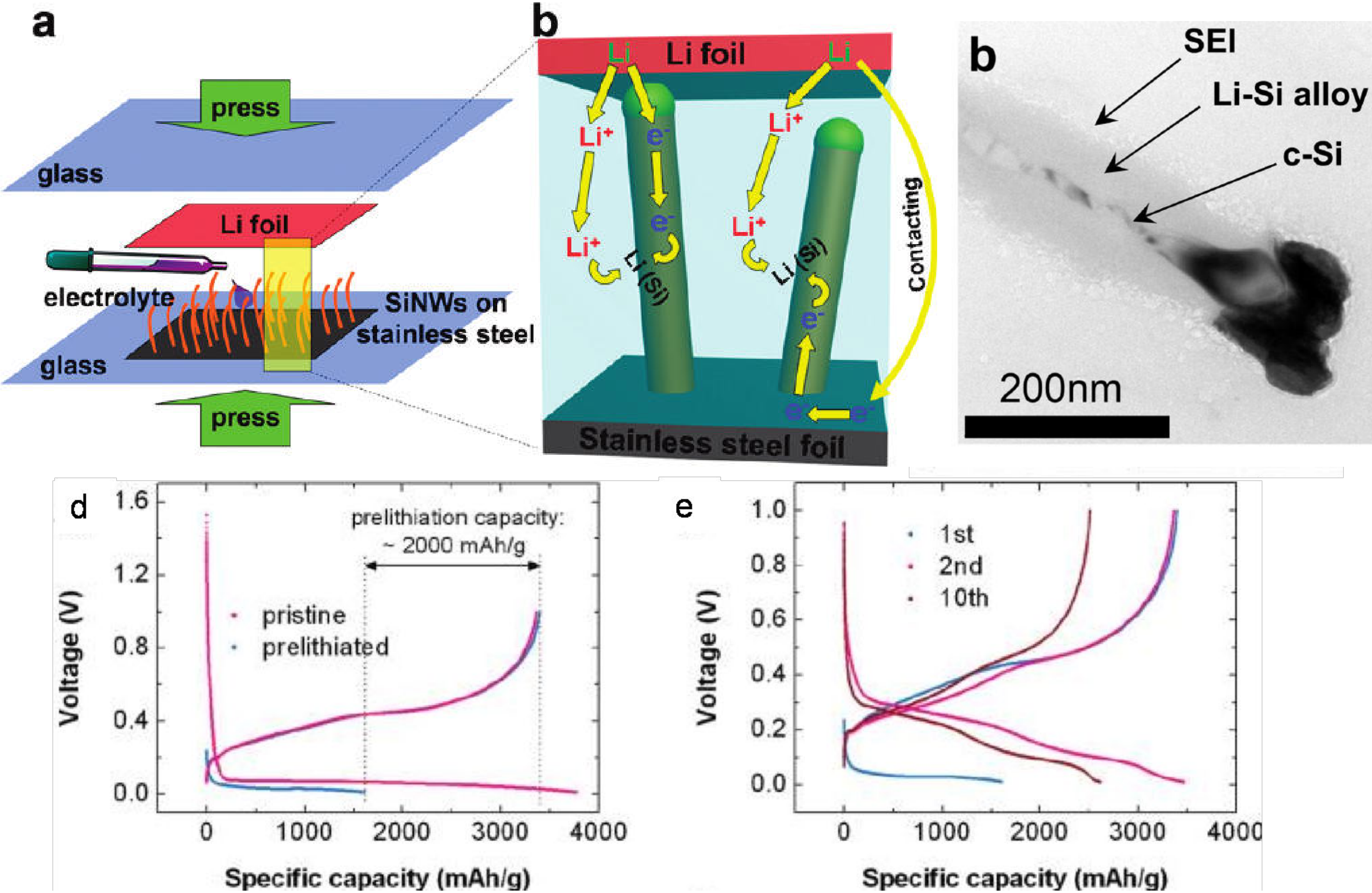
1) Ex-situ transmission electron microscopy
2) Ex-situ scanning electron microscopy
3) Ex-situ X-ray photoelectron spectroscopy
4) In operando X-ray diffraction and transmission X-ray microscopy

Electrochemical testing

1) Coin cells and pouch cells
2) A set of electrochemical techniques

Previous Accomplishments on Prelithiation

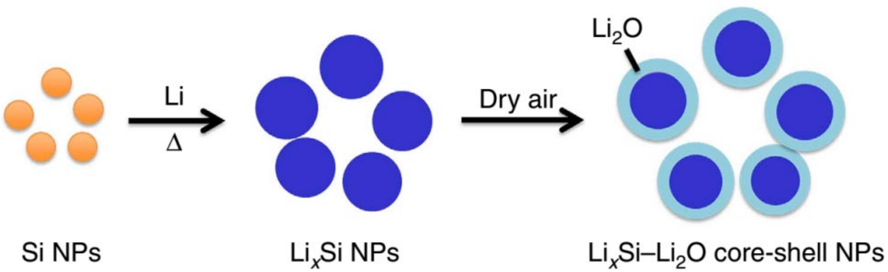
Prelithiation of Si nanowires via electrochemical shorting mechanism

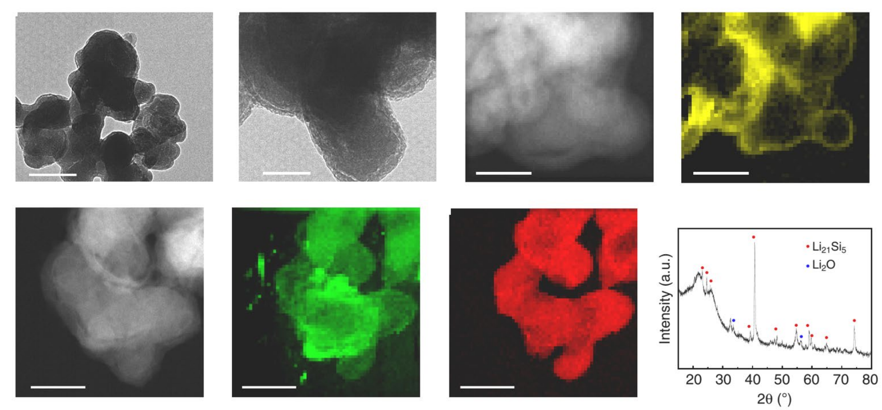


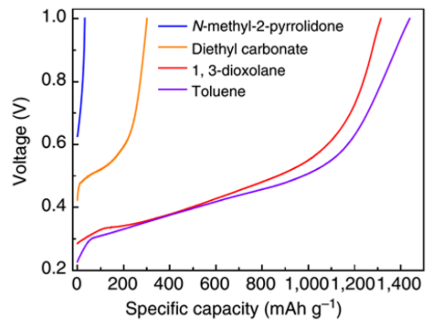
Cui group, *ACS Nano 5*, 6487 (2011)

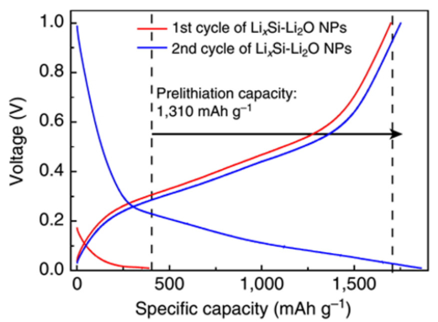
Accomplishment

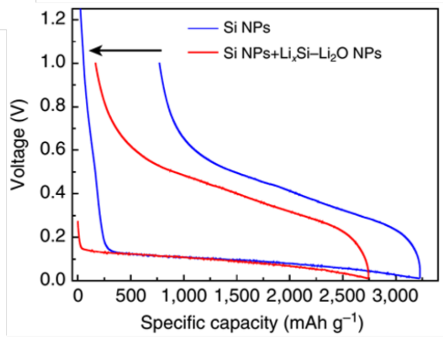
Dry-air-stable Li_xSi-Li_2O core-shell nanoparticles for anode prelithiation

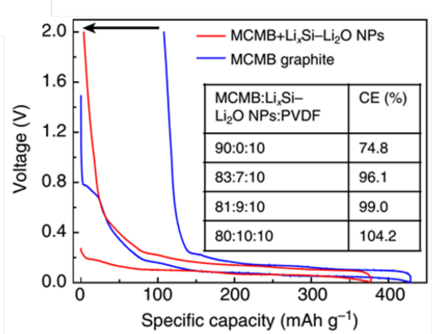


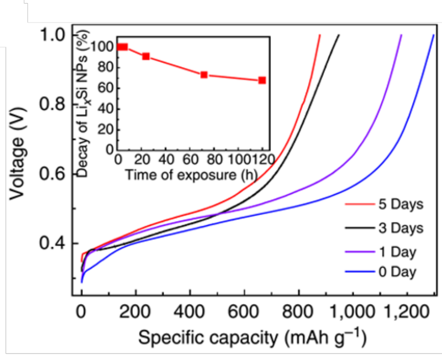


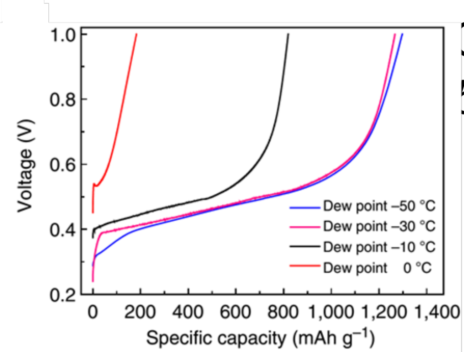








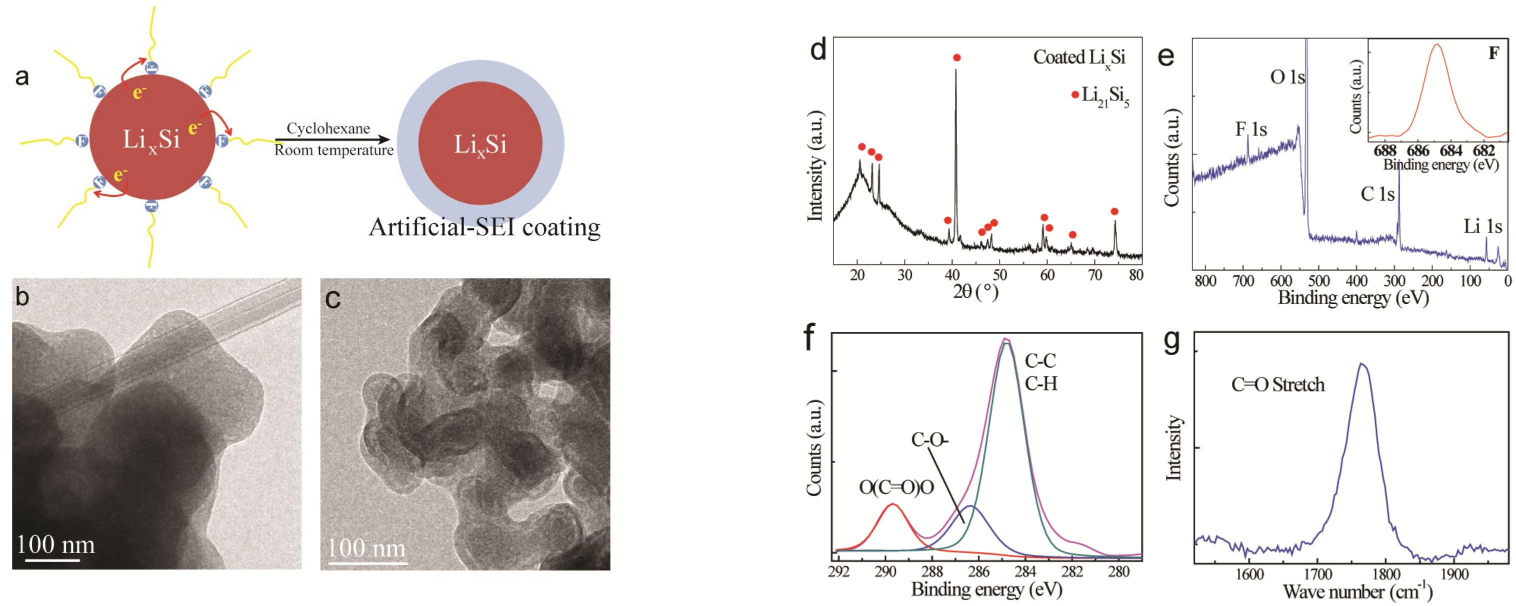


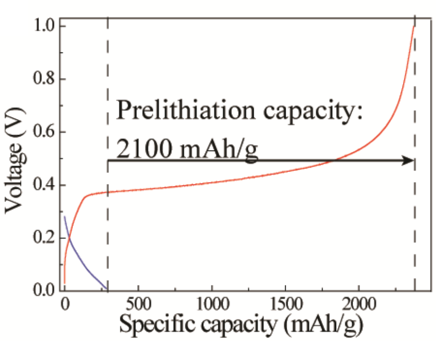


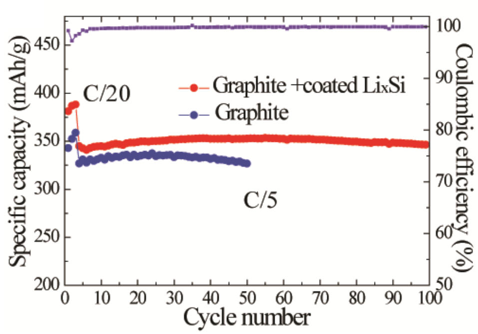
Cui group, *Nat. Commun*
5, 5088 (2014)

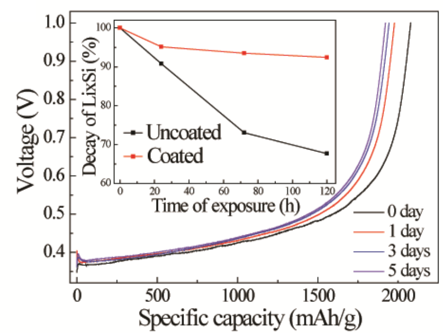
Accomplishment

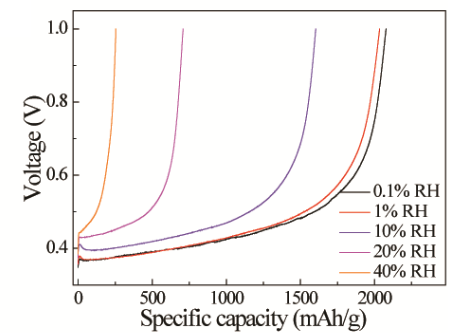
Artificial-SEI protected Li_xSi nanoparticles for anode prelithiation







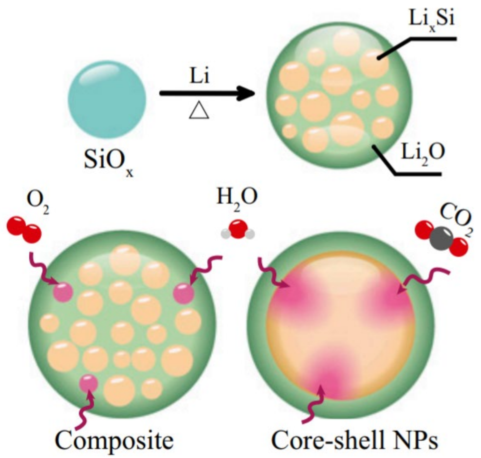


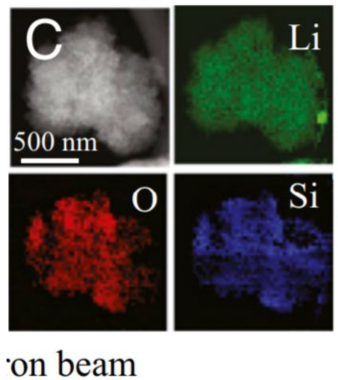


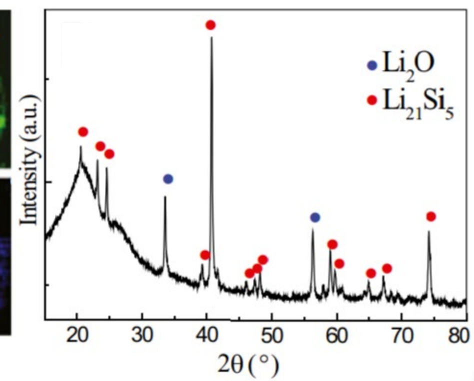
Cui group, *JACS*, 137, 8372 (2015) ***Spotlight***

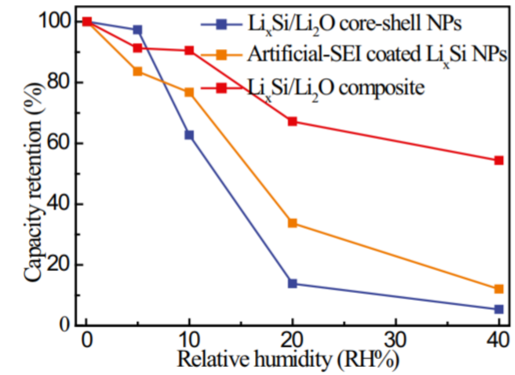
Accomplishment

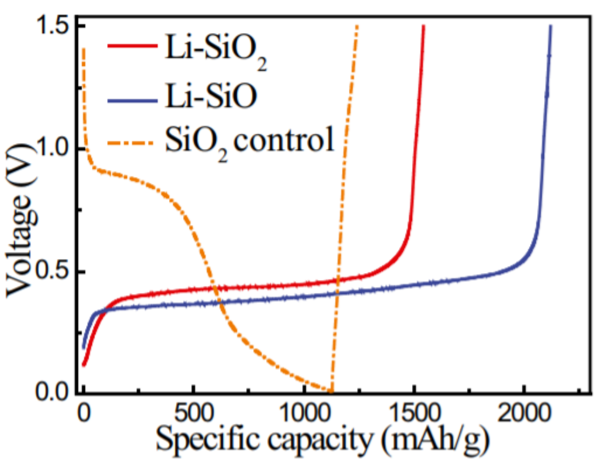
Metallurgically lithiated SiOx for anode prelithiation

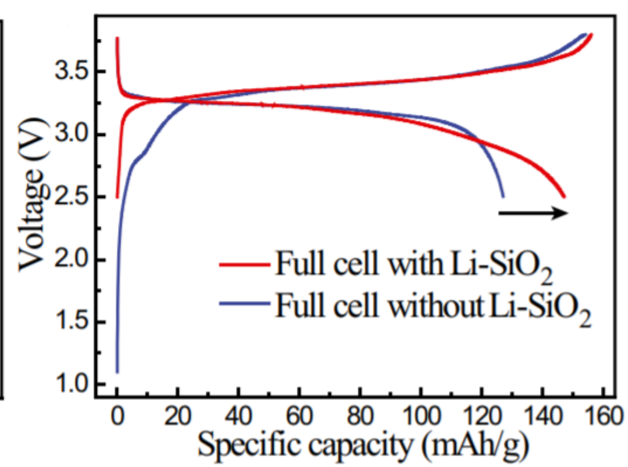


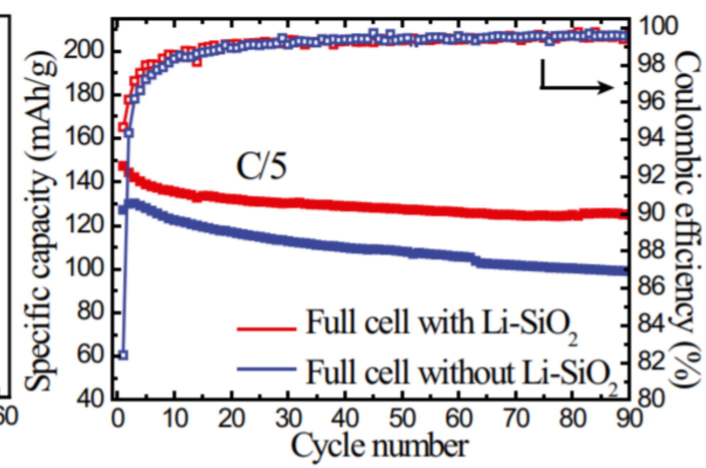








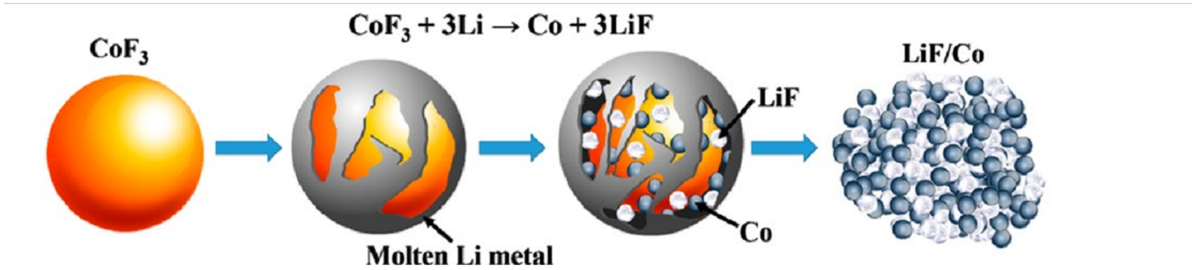


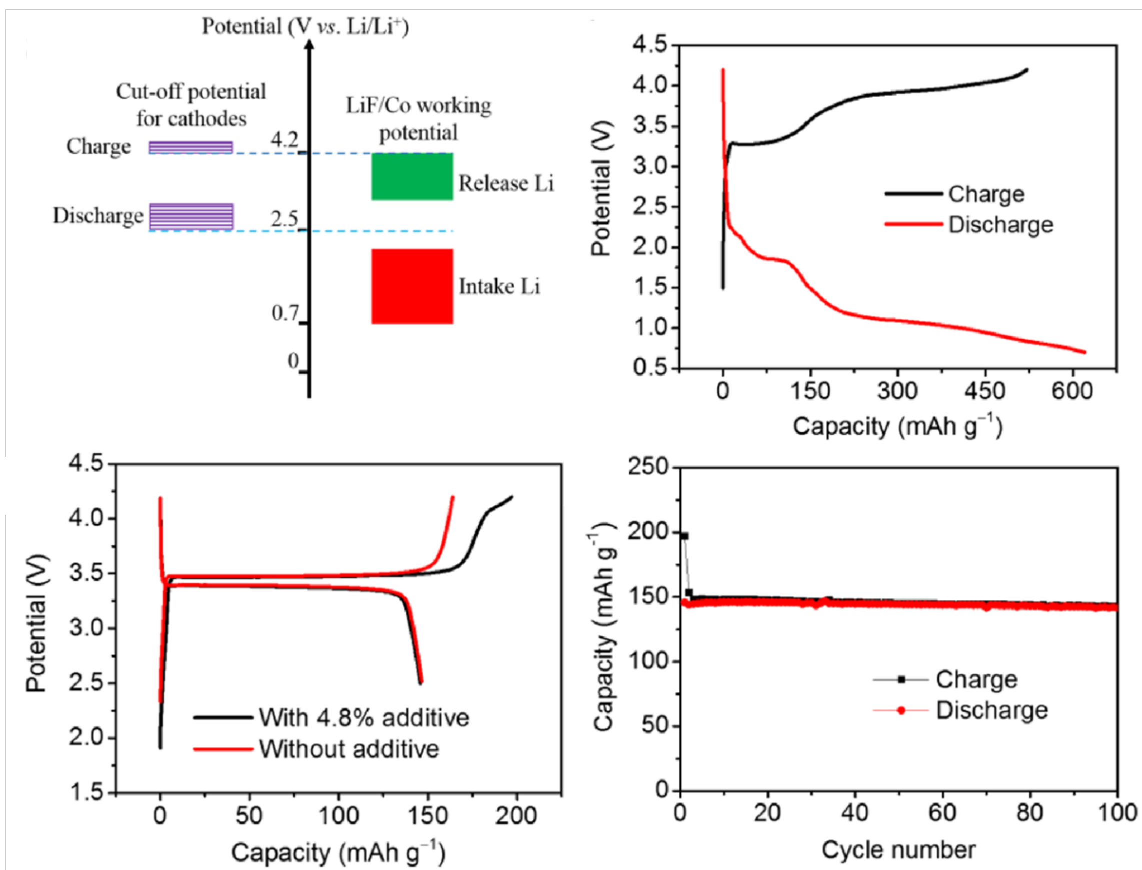


Cui group, *PNAS* 113, 7408 (2016)

Accomplishment

LiF/metal nanocomposite for cathode prelithiation

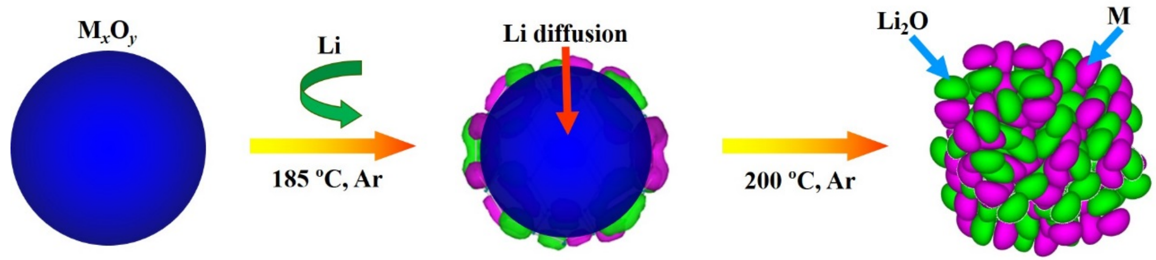




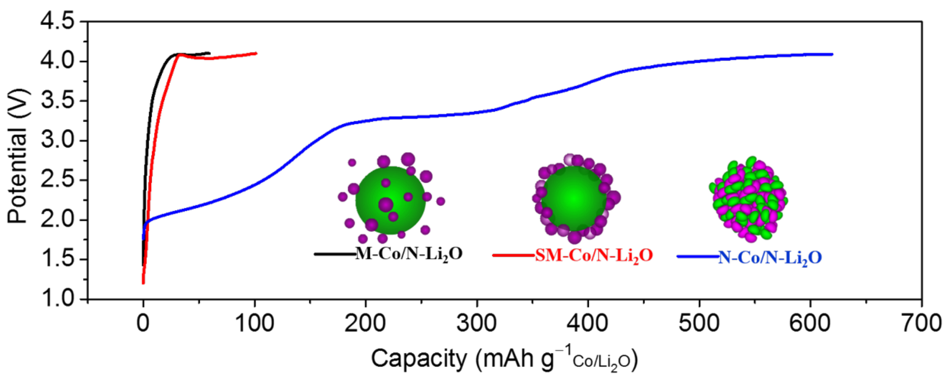
Cui group, *Nano Letters* 16, 1497 (2016)

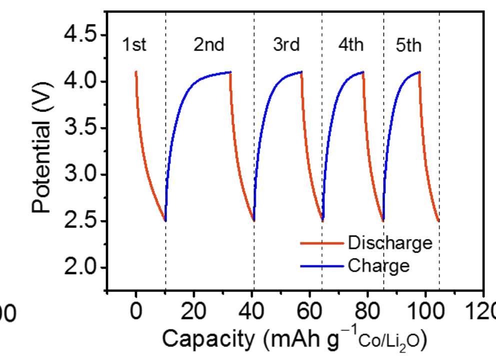
Accomplishment

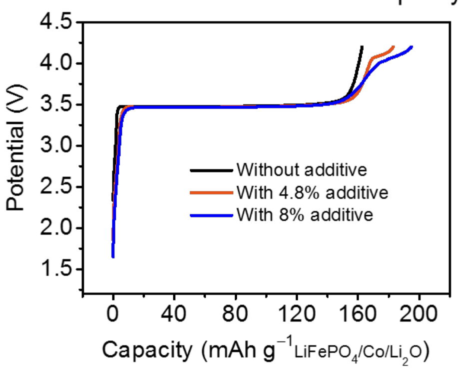
Li_2O/metal nanocomposite for cathode prelithiation

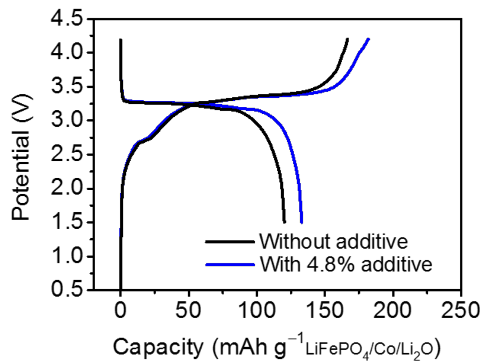


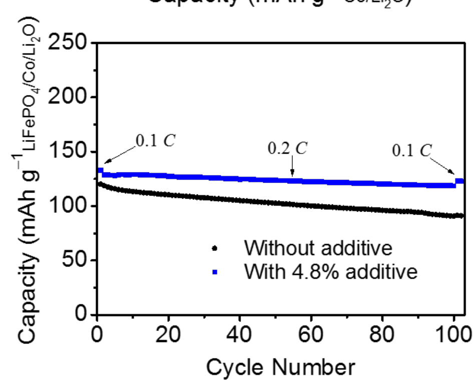
Cui group, *Nature Energy 1*, 15008 (2016)







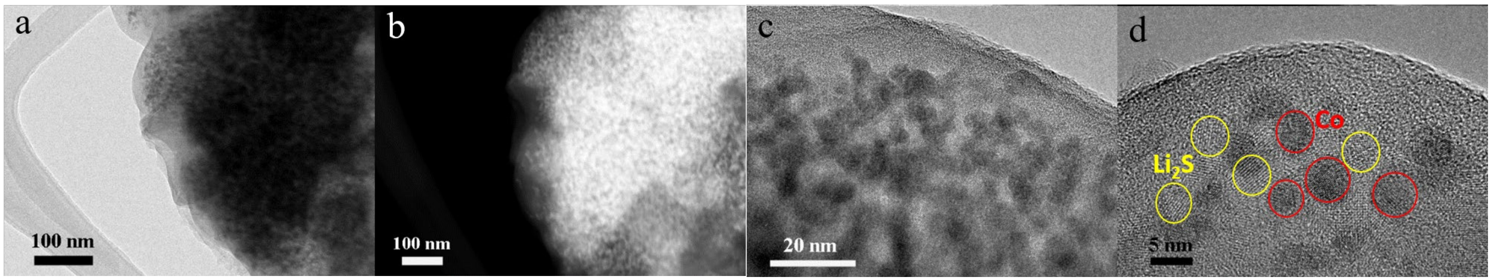


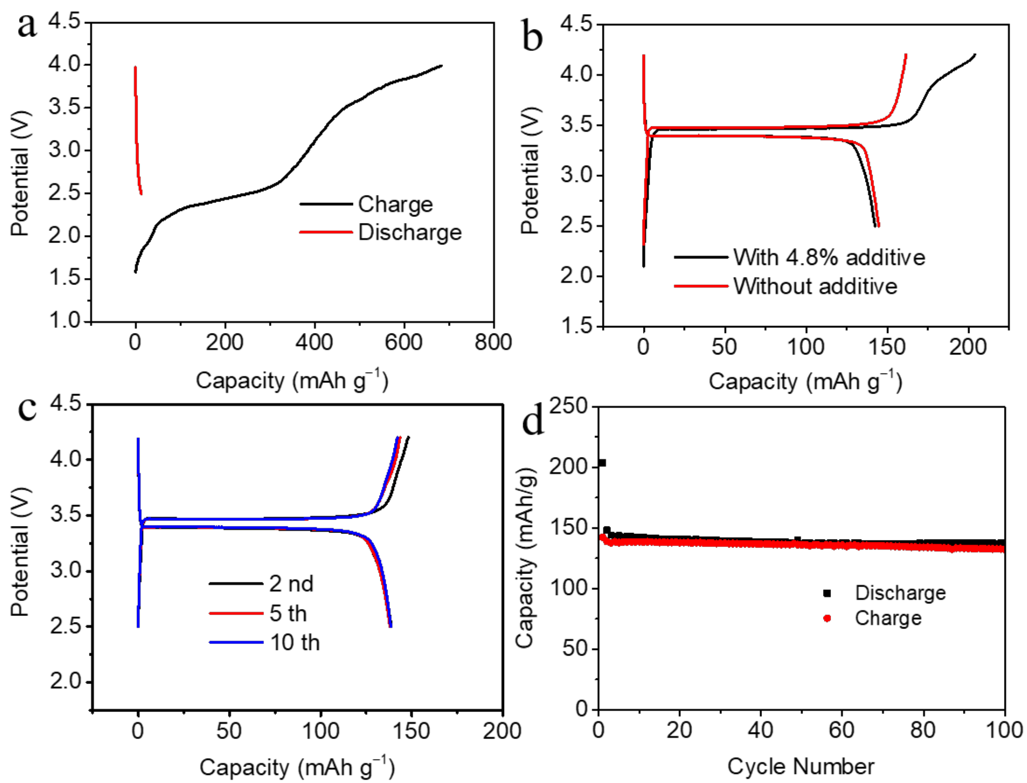


Accomplishment

Li_2S/metal nanocomposite for cathode prelithiation

$$Co + 2Li_2S \rightarrow CoS_2 + 4Li^+ + 4e^-$$

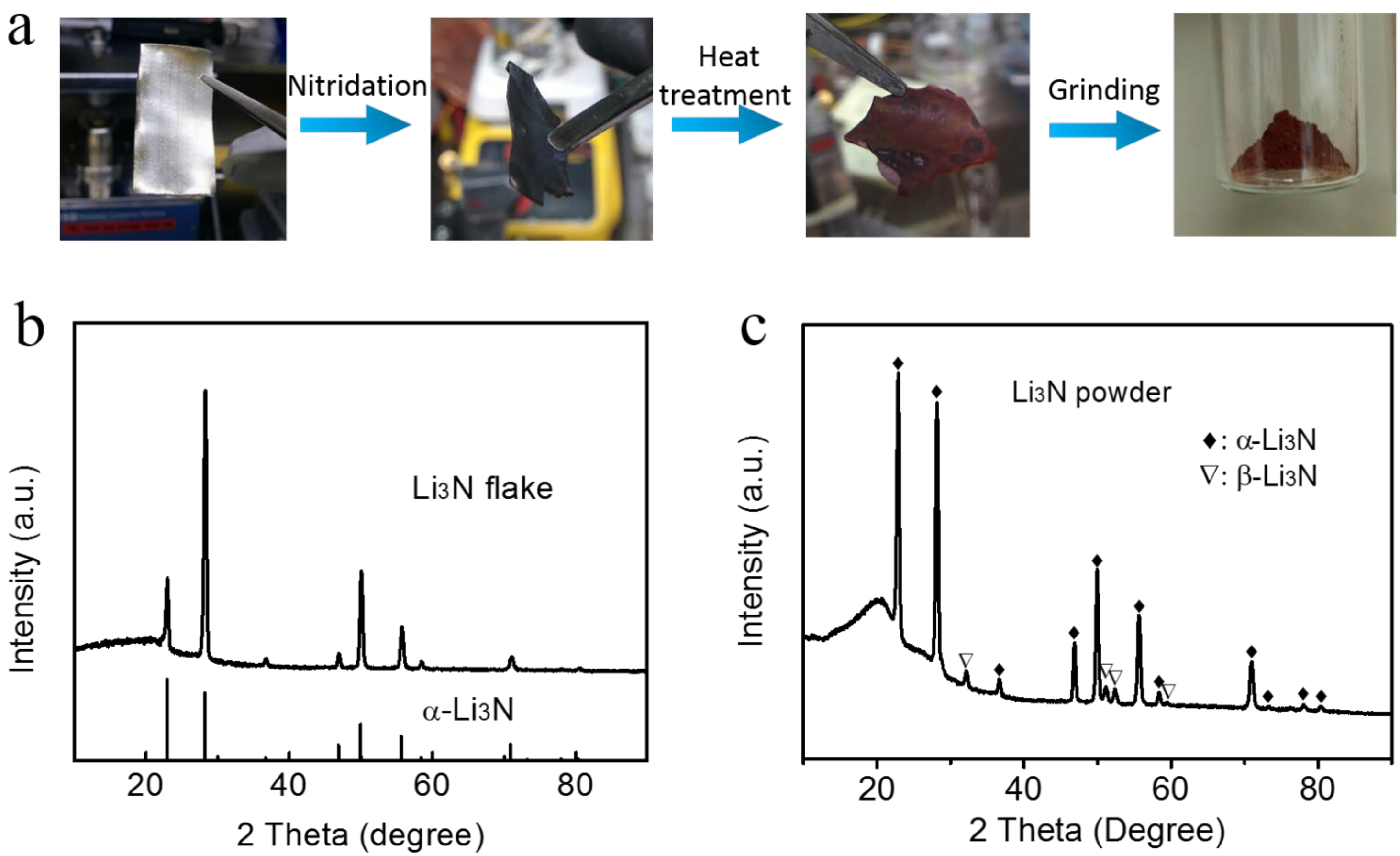




Cui group, *Advanced Energy Materials* 6, 1600154. (2016)

Accomplishment

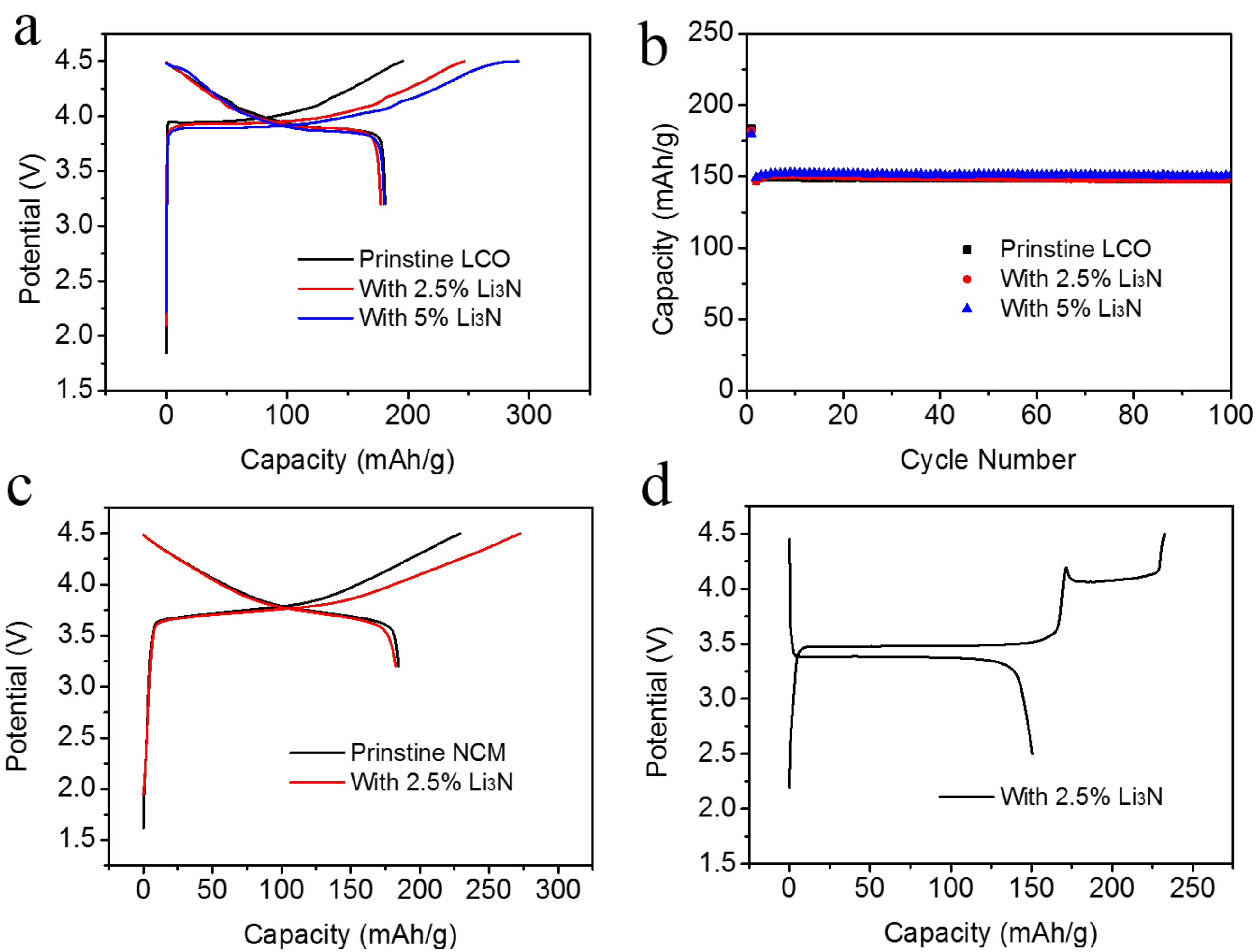
Li_3N nanocomposite for cathode prelithiation
-Synthesis and characterizations



Cui group, *Energy Storage Materials*, 6, 119 (2017)

Accomplishment

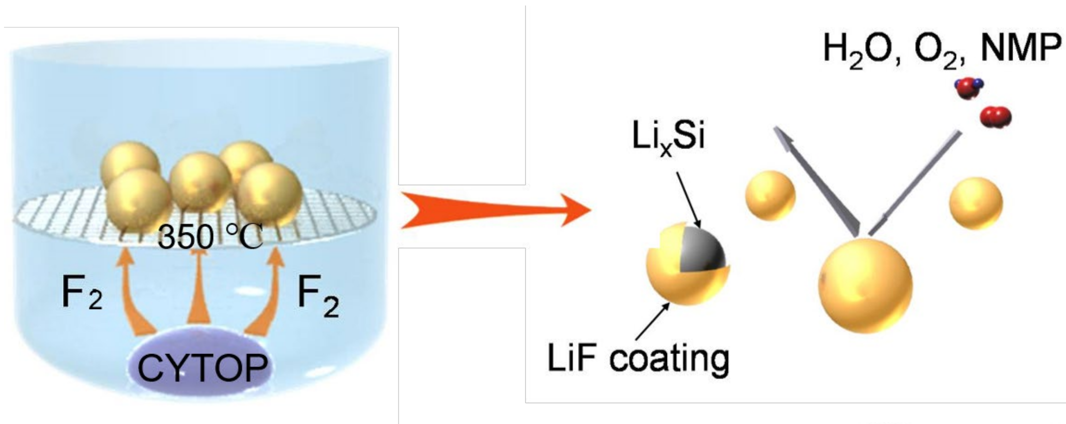
Li_3N nanocomposite for cathode prelithiation
- Battery performance

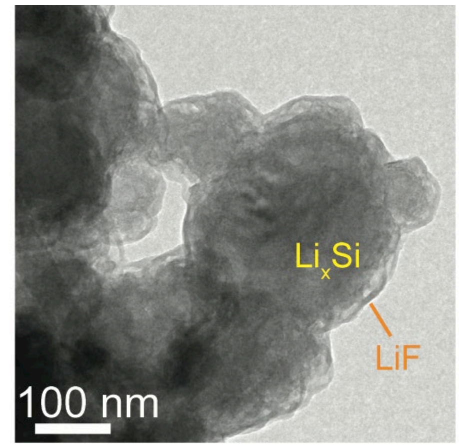


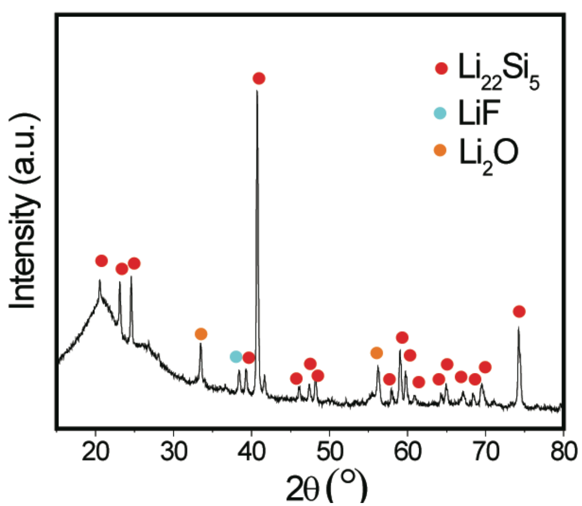
Cui group, *Energy Storage Materials*, 6, 119 (2017)

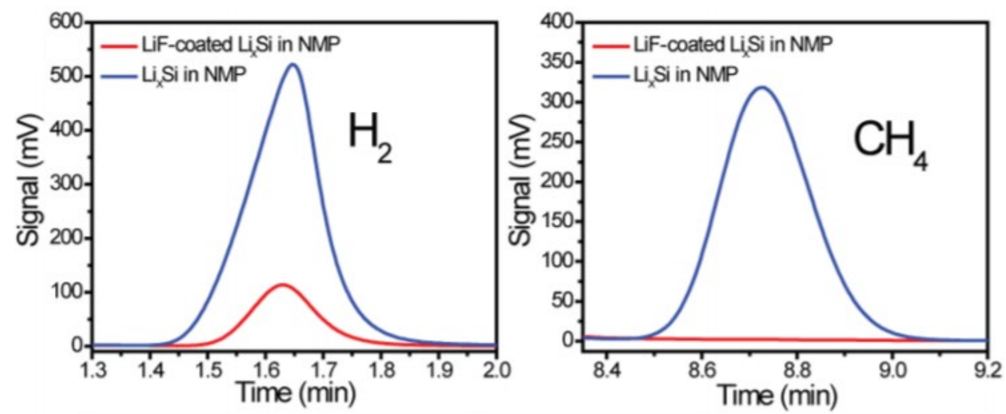
Accomplishment

NMP solvent-compatible Li_xSi-LiF core-shell nanoparticles for anode prelithiation
-Synthesis and characterizations







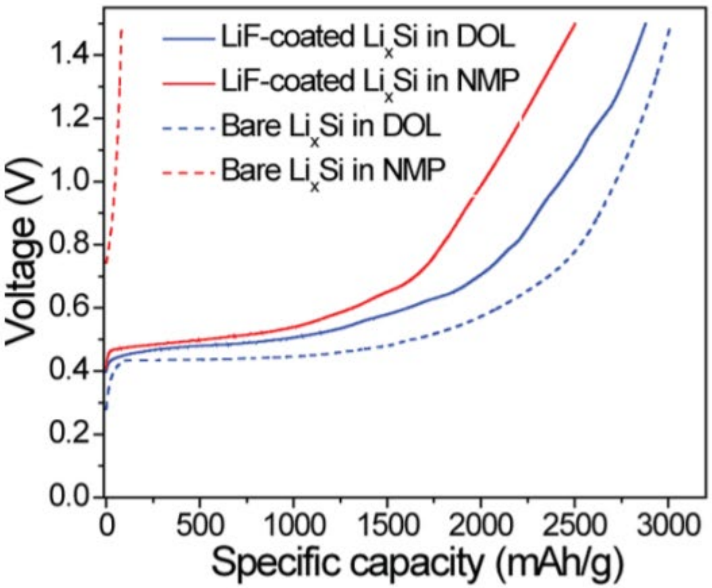


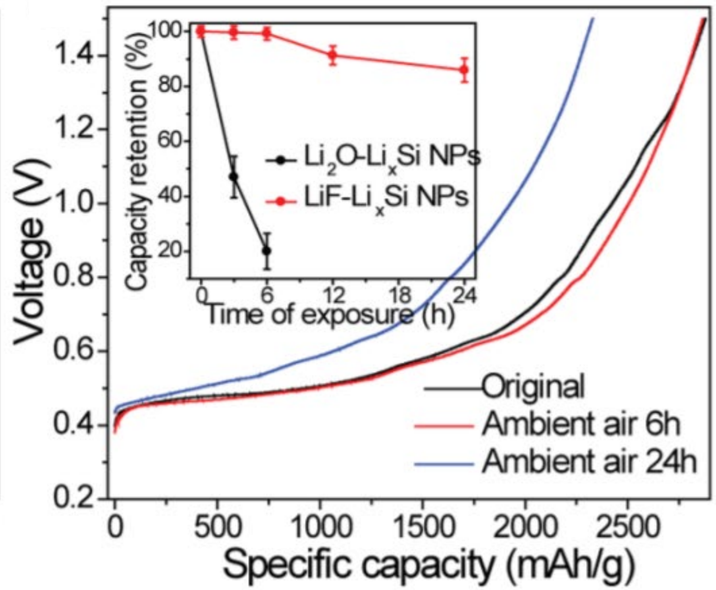
Reaction with NMP	H_2 (ppm)	CH_4 (ppm)
Li_xSi without LiF	18145	938
Li_xSi with LiF	2870	0

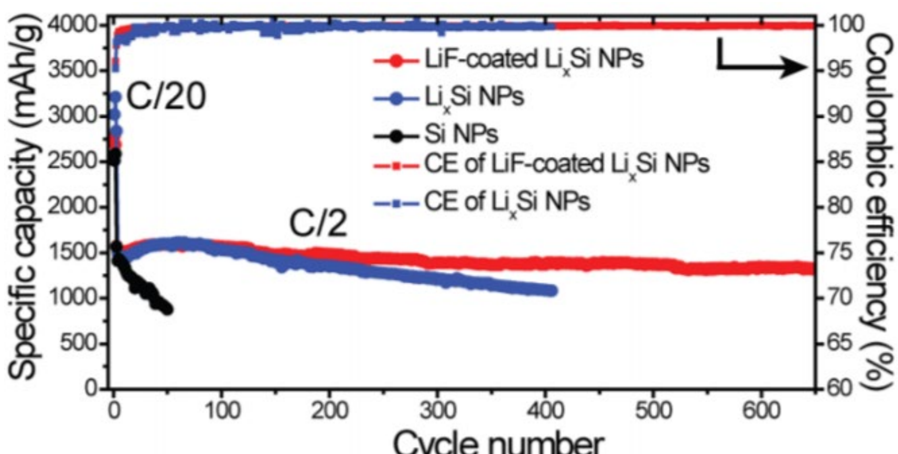
Cui group, *JACS* 139, 11550 (2017)

Accomplishment

NMP solvent-compatible Li_xSi-LiF core-shell nanoparticles for anode prelithiation -Battery performance



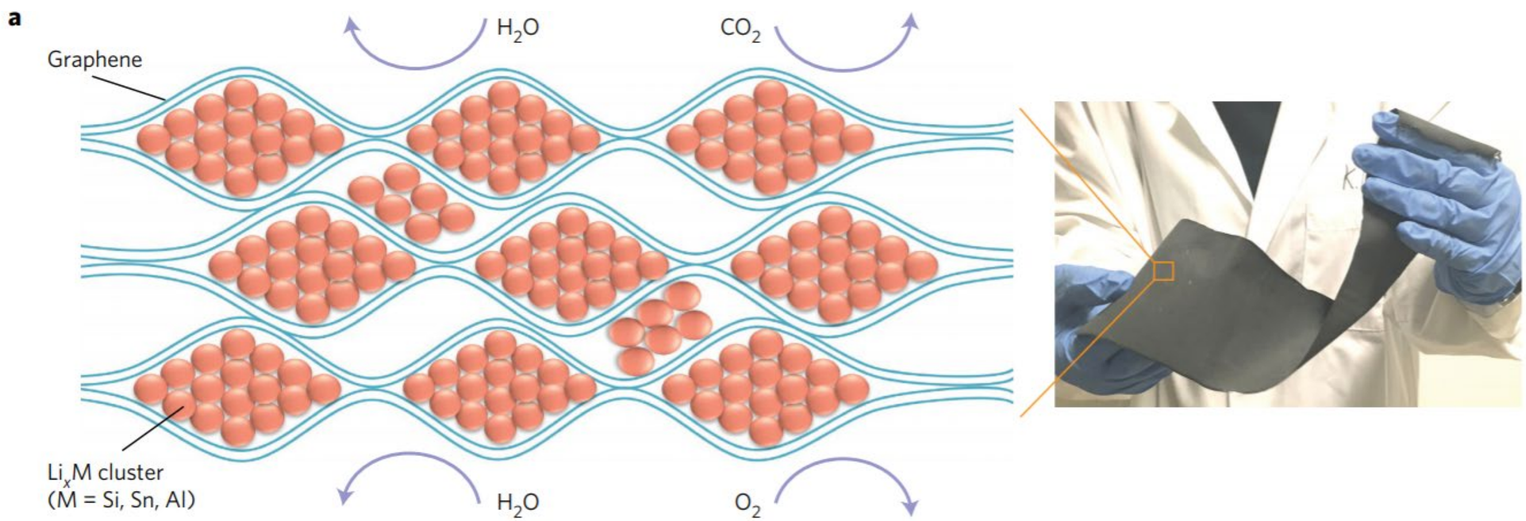


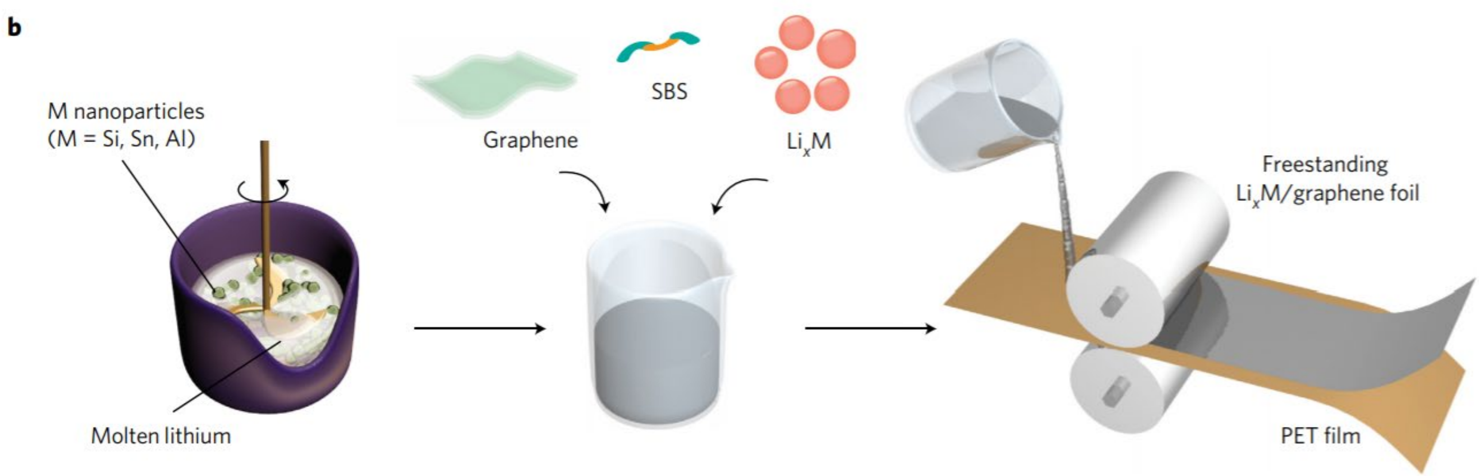


Cui group, *JACS* 139, 11550 (2017)

Accomplishment

Air-stable and freestanding lithium alloy/graphene foil for anode prelithiation
-Synthesis and characterizations

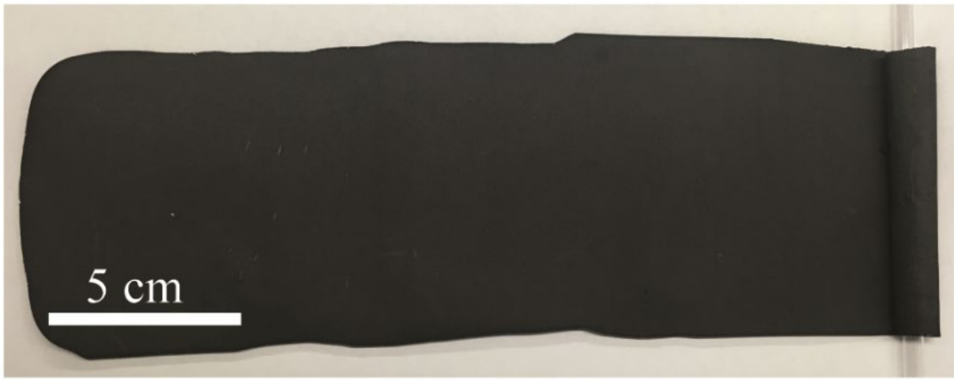


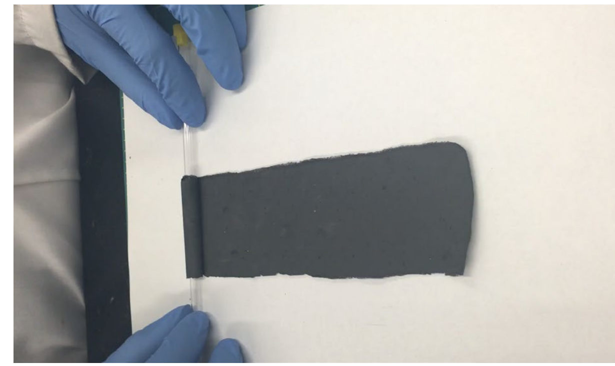


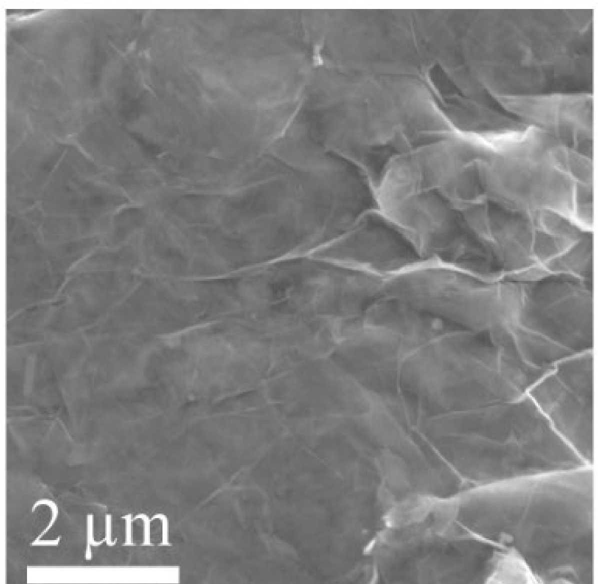
Cui group, *Nature Nanotechnology* 12, 993 (2017)

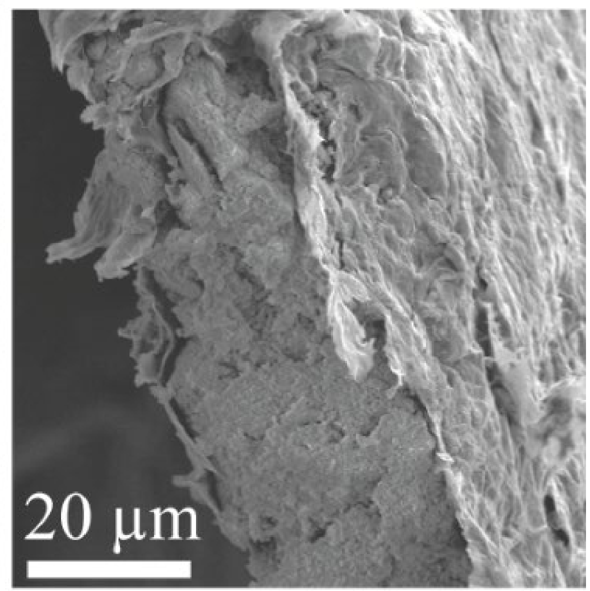
Accomplishment

Air-stable and freestanding lithium alloy/graphene foil for anode prelithiation
-Synthesis and characterizations





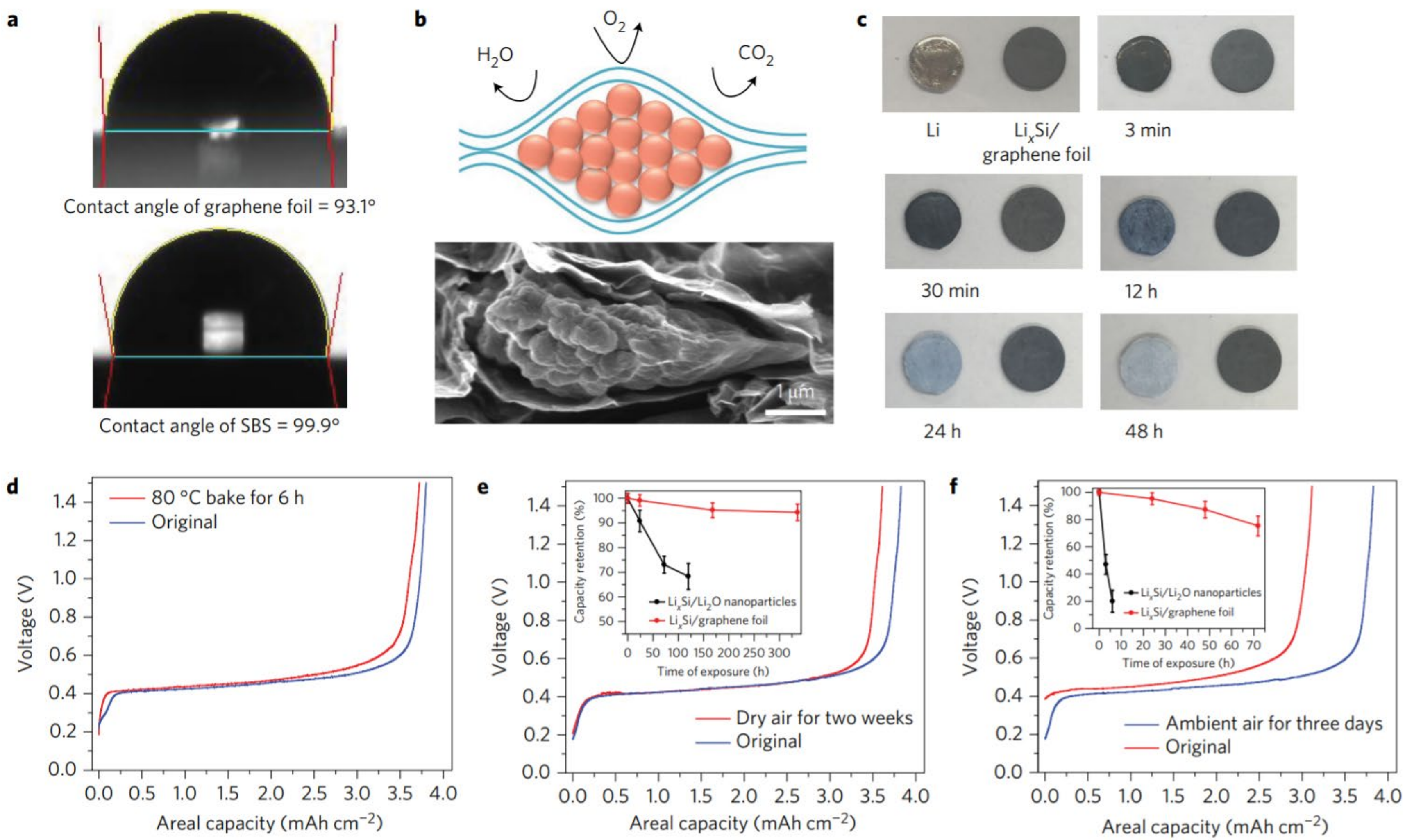




Cui group, *Nature Nanotechnology* 12, 993 (2017)

Accomplishment

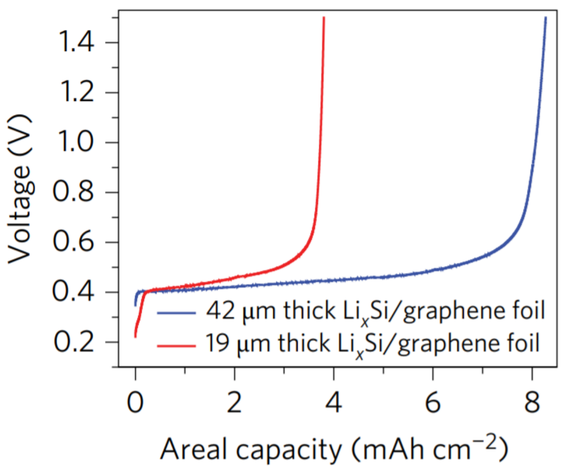
Air-stable and freestanding lithium alloy/graphene foil for anode prelithiation
-Stability in ambient air

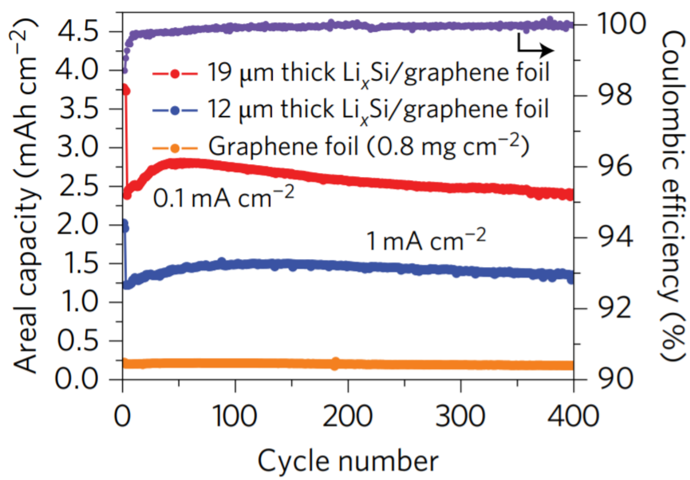


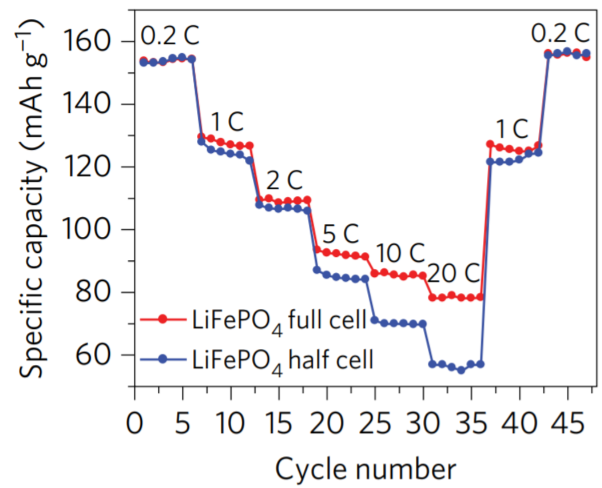
Cui group, *Nature Nanotechnology* 12, 993 (2017)

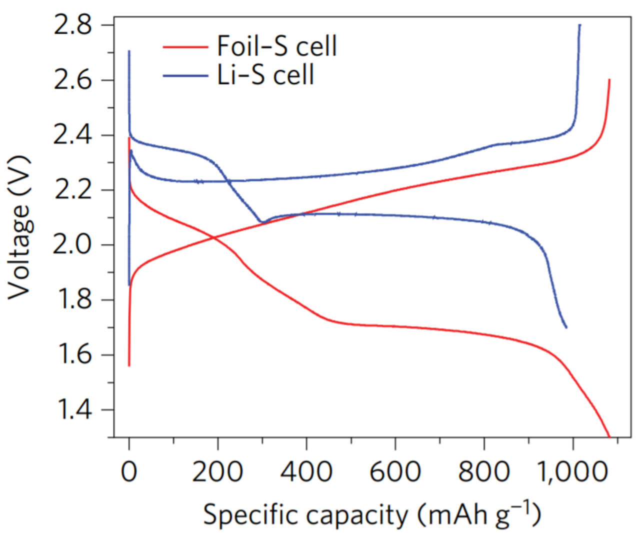
Accomplishment

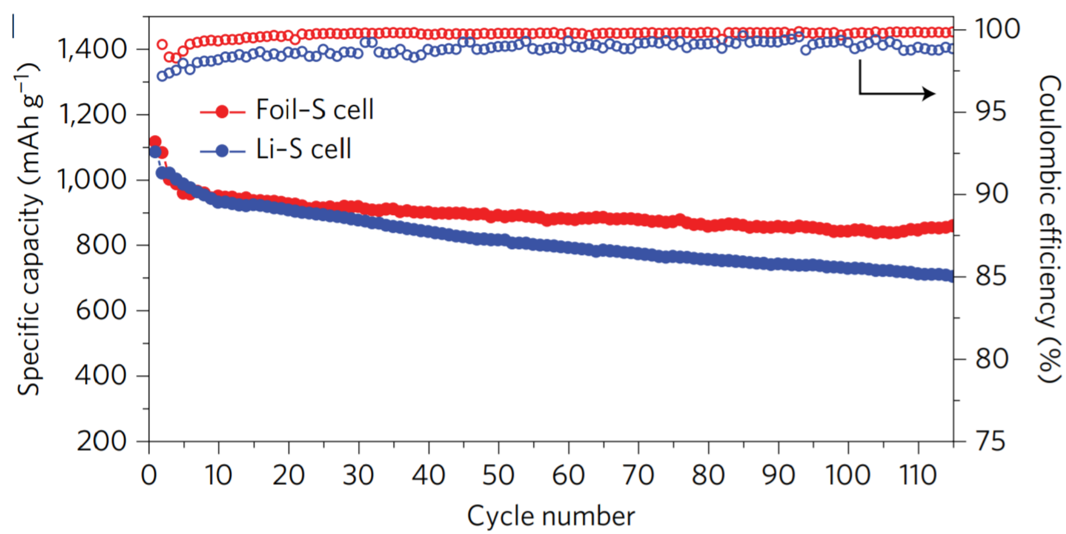
Air-stable and freestanding lithium alloy/graphene foil for anode prelithiation
-Battery performance







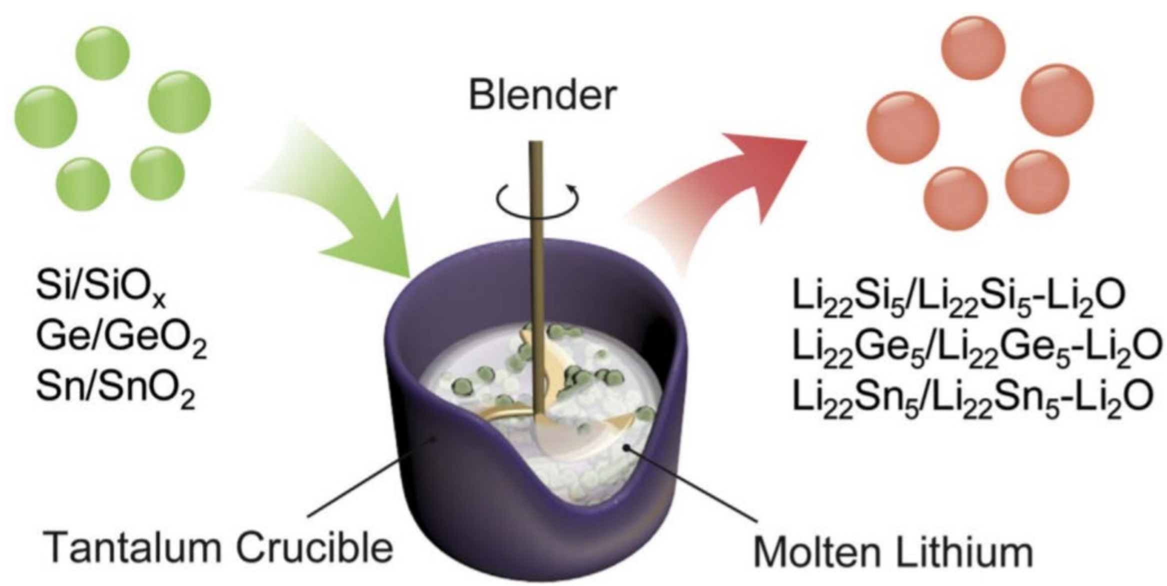


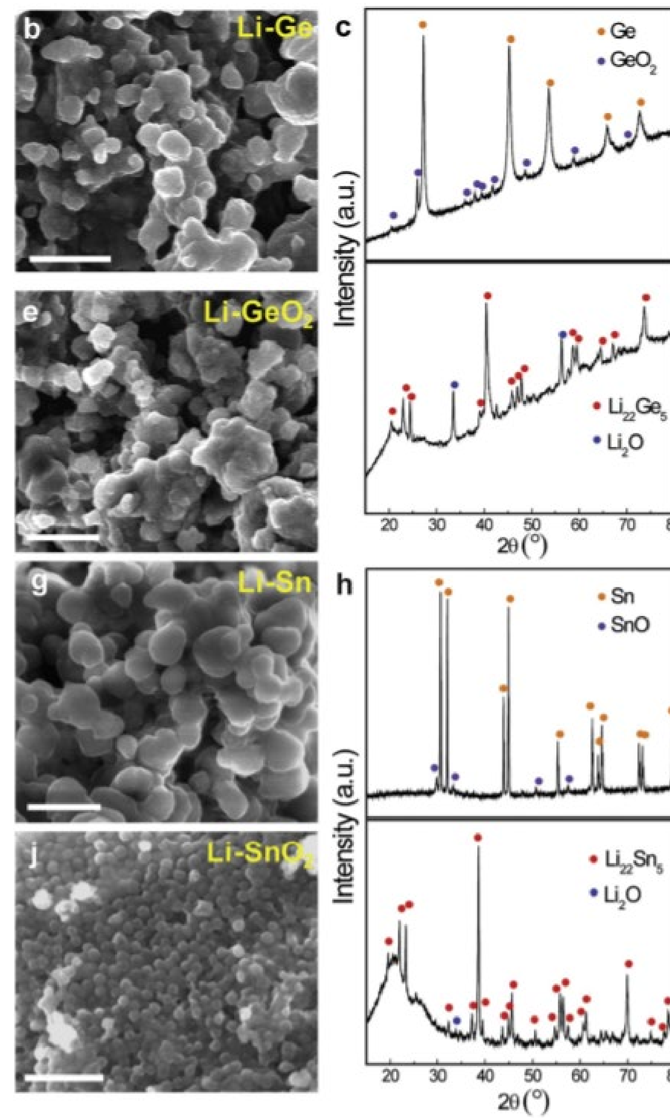


Cui group, *Nature Nanotechnology* 12, 993 (2017)

Accomplishment

General prelithiation approach for group IV elements and corresponding oxides
-Synthesis and characterizations

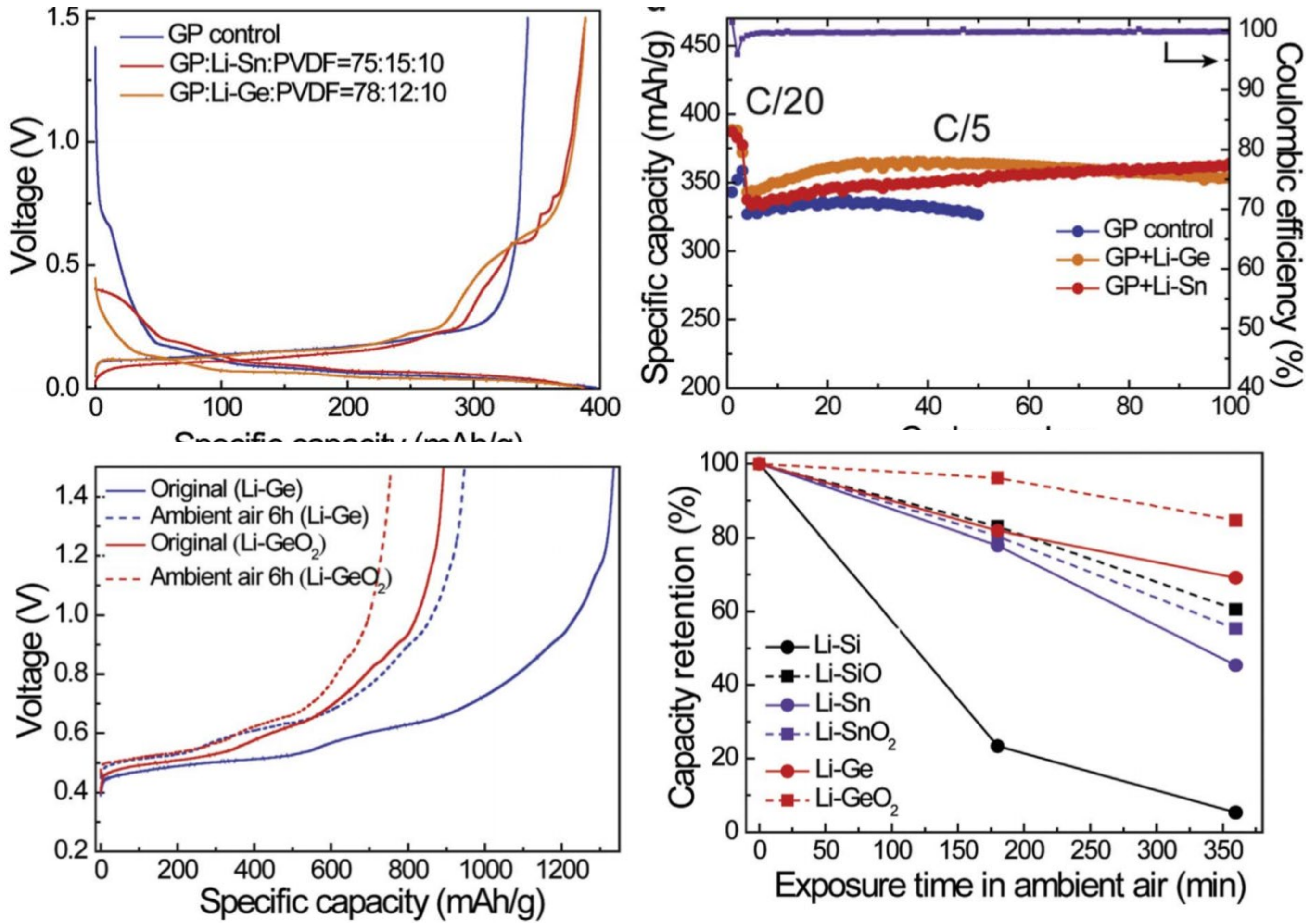




Cui group, *Energy Storage Materials*, 10, 275 (2018)

Accomplishment

General prelithiation approach for group IV elements and corresponding oxides
-Battery performance



Cui group, *Energy Storage Materials*, 10, 275 (2018)

Responses to Previous Year Reviewers' Comments

Not applicable

Collaboration and Coordination

SLAC: In-situ X-ray, Prof. Mike Toney

Companies: Amprius Inc.

Stanford: Professor Zhenan Bao

Remaining Challenges and Barriers

- It is difficult to fabricate Li-rich anode materials with fine structures and stable cycling.

- It is difficult to realize cathode prelithiation process to be compatible with solvent processing.

- It is difficult to realize prelithiation process at the electrode level.

Proposed Future Work

- To improve the stability of prelithiation reagents in the slurry process by developing new solvent-binder combination.
- To improve the stability of prelithiation reagents in the ambient air condition by exploring different kinds of coatings and nanostructures.
- To explore other materials with high prelithiation capacity and stability.
- To understand the interaction between molecule in the air and different coatings of the prelithiation reagents.
- To synthesize Li-rich anode materials with fine structures and stable cycling and then pair them with high capacity Li-free cathode materials.
- To explore the prelithiation process at the electrode level instead of particle level through a facile method.

Summary

- **Objective and Relevance:** The goal of this project is to increase 1st cycle Coulombic efficiency of lithium ion batteries via both anode and cathode prelithiation.
- **Approach/Strategy:** This project combines advanced materials synthesis, characterization, battery assembly and testing, which has been demonstrated to be highly effective.
- **Technical Accomplishments and Progress:** This project has produced many significant results, meeting milestones. They include identifying the key issues in prelithiation, using rational materials design, synthesizing and testing, and developing scalable and low-cost methods. The results have been published in top peer-reviewed scientific journals. The PI has received numerous invitations to speak in national and international conferences.
- **Collaborations and Coordination:** The PI has established a number of highly effective collaborations.
- **Proposed Future Work:** Rational and exciting future has been planned.

59. (Invited) "Nanoscale Design and Cryogenic Electron Microscopy for Energy Storage", American Chemical Society Spring Meeting, New Orleans, March 18-22, 2018.
60. (Invited) "Emerging Materials Selection and Design for Batteries with High Energy Density, Ultralong Cycle Life and Excellent Safety", International Battery Seminar, Fort Lauderdale, March 26-29, 2018.
61. (Invited) "Materials design of Li-metal host and interface and characterization with cryo electron microscopy", US-Germany Energy Storage Workshop, Washington DC, March 26-27, 2018.
62. (Invited) "Nanoscale Design and Cryogenic Electron Microscopy for of Energy Storage", Materials Research Society Spring Meeting, Symposium EN14, Phoenix, Arizona, Apr 2-6, 2018.
63. (Invited) Yi Cui "New Battery Technology for Electrical Vehicles and Grid Scale Energy Storage" the 2018 US-China Green Energy Summit (2018UCGES), Aug 3-4, 2018, Hyatt Regency, San Francisco Airport.
64. (Invited) "How Far Can Batteries Go" Global Energy Forum, Stanford University, Nov. 1-2, 2018.
65. (Invited) "Nanoscale Design for Lithium-Sulfur Batteries", Materials Research Society Fall Meeting, Symposium ET09, Boston, Nov. 25-30, 2018.
66. (Invited) "Nanoscale Composite Polymer Electrolyte Batteries", Symposium ET01 Materials Research Society Fall Meeting, Boston, Nov. 25-30, 2018.
67. (Invited) "Nanotechnology for Energy, Environment and Textile", Seminar, Peking University School of Materials Science at Shenzhen, China, Jan 14, 2018.
68. (Invited) "Nanotechnology for Energy, Environment and Textile", seminar, Dalian Institute of Chemical Physics, Dalian, China, Jan 16, 2018.
69. (Invited) "Nanotechnology for Energy, Environment and Textile", seminar, Dalian Institute of Technology, Dalian, China, Jan 19, 2018.
70 (Invited) "Nanotechnology for Energy, Environment and Textile", seminar, UC Irvine, Feb. 2, 2018.
71 (Invited) "Pathways of Batteries Towards Sustainable Electric Transportation and Stationary Storage", Stanford Energy Seminar, Stanford University, Feb. 12, 2018.
72. (Invited) "Nanotechnology for Energy, Environment and Textile", seminar, Tsinghua University, Beijing, China, Mar 5, 2018.
73. (Invited) "Nanotechnology for Energy, Environment and Textile", seminar, Beijing Institute of Technology, Beijing, China, Mar 5, 2018.
74. (Invited) "Nanotechnology for Energy, Environment and Textile", seminar, China National Center of Nanotechnology, Beijing, China, Mar 6, 2018.
75. (Invited) "Nanotechnology for Energy, Environment and Textile", seminar, Institute of Processing, Chinese Academy of Sciences, Beijing, China, Mar 6, 2018.
76. (Invited) "Nanotechnology for Energy, Environment and Textile", seminar, University of Science and Technology of Beijing, Beijing, China, Mar 7, 2018.
77. (Invited) "Nanotechnology for Energy, Environment and Textile", seminar, Research Institute of China Petroleum, Beijing, China, Mar 7, 2018.
78. (Invited) "Nanotechnology for Energy, Environment and Textile", seminar, Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, China, Mar 8, 2018.
79. (Xinda Lectureship) "Nanotechnology for Energy, Environment and Textile", Peking University, Beijing, China, Mar 9, 2018.
80 (Invited) "Materials Design for High Energy Batteries towards Electric Transportation", seminar, General Motors, Warren, Michigan, March 16, 2018.

81 (Invited) "Nanomaterials Design for Energy Storage and Catalysis" Northwestern University, Materials Science Seminar, Oct. 2, 2018.
82. (Invited) "Batteries Now and Future". The Stanford Chinese Faculty & Family Club (SCFFC), Quarterly Speaker Series, Nov. 4, 2018.